

PATENT SPECIFICATION

NO DRAWINGS

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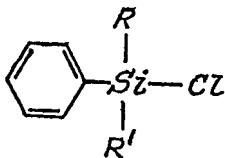
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COMPLETE SPECIFICATION

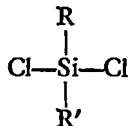
Partial Phenylation of Chlorosilanes

We, FARBENFABRIKEN BAYER AKTIEN-
GESELLSCHAFT, a body corporate organised
under the laws of Germany, of Leverkusen,
Germany, do hereby declare the invention,
5 for which we pray that a patent may be
granted to us, and the method by which it
is to be performed, to be particularly de-
scribed in and by the following statement:—

10 This invention relates to the partial
phenylation of chlorosilanes, and is especially
concerned with the controlled production of
phenyl-substituted organo-chlorosilanes of the
general formula



15 in which each of the substituents R and R'
(same or different) is a chlorine atom, a
phenyl radical or an alkyl radical, which
may be cyclic, having 1 to 24 carbon atoms,
especially a methyl radical, by phenylation of
20 a chlorosilane of the general formula



It is known to carry out this phenylation
with cooling, for example to temperatures
between -5 and -17°C , by means of a
25 suspension of sodium-phenyl in an inert dis-
persing agent, but this method has hitherto
not achieved any technical importance be-
cause the reaction could not be sufficiently
controlled. Instead of a phenylation graded
30 in accordance with the desired product, there

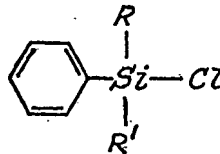
[Price 4s. 6d.]

were mainly obtained the almost useless tetra-
organosilanes, at best in admixture with tri-
organo-monochlorosilanes which are generally
not much in demand. Referred to the silane
used and, in particular, to the sodium-phenyl, 35
which cannot be recovered even when an ex-
cess is used, the yields of monophenyl tri-
chlorosilane obtained from silicon tetra-
chloride by the method hitherto used, and
also of the usually especially desired diorgano-
dichlorosilanes obtained from silicon tetra-
chloride or a monoorgano-trichlorosilane, are
unsatisfactory. 40

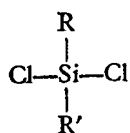
Also, in a one-step reaction according to
Wurtz-Fittig using sodium and chlorobenzene 45
without the previous preparation of sodium-
phenyl, which is more difficult to carry out,
silicon tetrachloride can only be converted
into phenyl-trichlorosilane, diphenyl-dichloro-
silane and triphenyl-chlorosilane in propor-
50 tion of about 5 to 17% each, whereas the
remainder is perphenylated.

It has now been found that a higher pro-
portion of silanes of a pre-determined degree
of phenylation, i.e. in particular a low 55
degree of phenylation, can be achieved by
observing a combination of definite reaction
conditions, in that cooling and stirring of the
silicon compound are carried substantially
further than has hitherto been proposed and
60 that the addition of the phenylating agent is
delayed.

According to the invention a process for
the controlled production of silane derivatives
of the general formula 65



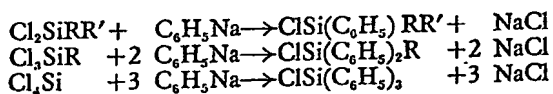
wherein the substituents R and R' are as aforesaid, comprises providing a solution of a silane derivative of the general formula



- 5 in an inert solvent, providing a suspension of sodium-phenyl in an inert dispersing medium in a concentration of at most 1 mol $\text{C}_6\text{H}_5\text{Na}$ per litre, cooling the silane derivative solution to a temperature of between -20 and -80°C whilst stirring vigorously, and simultaneously adding to the silane derivative solution an amount of the suspension stoichiometrically corresponding to the desired degree of phenylation, the addition of the suspension taking place evenly over a period of at least 30 minutes, and being effected in the absence of air and water.

- 20 The silane derivative solution is suitably provided by dissolving the silane derivative in at least an equal volume of the inert solvent.

Preferably the suspension is added over



- 55 The period of time of at least 30 minutes, during which the phenylating agent is added to the chlorosilane solution, may also exceed 3 hours, but this presents no particular economic advantage.

- 60 Aromatic, aliphatic and cycloaliphatic hydrocarbons are suitable for diluting the silane derivatives, and examples of suitable diluents are benzene, toluene, xylene, hexane and cyclohexane. Solvents which are electron donors, such as dialkyl ethers, cyclic ethers and trialkylamines, can also be used for this purpose, especially in admixture with hydrocarbons.

- 70 The same solvents can be used for dispersing the sodium, provided that their boiling point is higher than the melting point of the metal (about 97°C); in the case of ethers, however, it should be noted that they may react, when in prolonged contact with sodium-phenyl, to form alcoholates.

- 75 During the process as well as during the preparation of the sodium-phenyl, the access of air or water must be excluded. It is therefore advantageous to use a protective atmosphere of inert gas, such as very pure nitrogen or argon, which may, if desired, be at super-atmospheric pressure. Isolation of the phenylation products is performed by known methods.

a period of 1 to 3 hours, and preferably the suspension is also cooled. The preferred temperature of the solution is between -20 and -40°C .

The sodium-phenyl suspension may be obtained in known manner from sodium and chlorobenzene, for example by introducing 92 g. of the metal in small pieces into 2 litres of toluene or another suitable dispersing agent with the exclusion of air, heating the mixture to the melting point of sodium and dispersing it, for example by means of a vibrating mixing device, allowing the mixture to cool to 10°C , adding 224 g. chlorobenzene dropwise while cooling to 10 to 15°C , and continuing the mixing for a further 1 to 2 hours. The suspension used in the Examples described below was obtained thus, and had a concentration of 0.82 mol $\text{C}_6\text{H}_5\text{Na}$ per litre. The concentration of sodium-phenyl in the suspension can be reduced to any extent, economic consideration being the only limit.

Depending upon the silane derivative to be phenylated and the desired silane derivative, there is used a quantity of the sodium-phenyl suspension such that 1, 2 or 3 molecules of $\text{C}_6\text{H}_5\text{Na}$ are used for every silicon atom, as shown by the following reaction equations:—

The following Examples are given for the purpose of illustrating the invention.

EXAMPLE 1.

292 grams diphenyl-dichlorosilane and 292 g. toluene are introduced, with the exclusion of air and moisture, into a flask fitted with stirrer, thermometer and dropping funnel. The contents of the flask are cooled externally to -20°C and 1 litre of the sodium-phenyl suspension described above is added dropwise with intense stirring over a period of 2 hours. Cooling is then interrupted and the reaction mixture is further stirred for 1 to 2 hours. The mixture is then heated to 100°C , filtered hot with the exclusion of air, the sodium chloride remaining on the filter is washed with a little hot toluene, and the solvent is evaporated off from the combined filtrates. The desired triphenyl-chlorosilane is obtained from the residue by fractional distillation under a pressure of 0.2 mm Hg in a yield of 88% referred to the sodium-phenyl used.

EXAMPLE 2.

Using the process steps described in Example 1 a mixture of 264 g. phenyl-trichlorosilane and 264 g. toluene is reacted at -30°C with 1 litre of the sodium-phenyl suspension described above. The yield of diphenyl-di-

chlorosilane amounts to 82% referred to the sodium-phenyl used.

EXAMPLE 3.

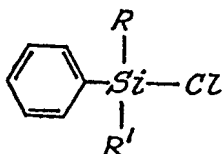
- Again using the process described in Example 1 a mixture of 100 g. silicon tetrachloride, 675 cc dioxan and 675 cc toluene is reacted at -30°C with 1 litre of the sodium-phenyl suspension. The desired diphenyl-dichlorosilane is obtained in a yield of 61.5% referred to the sodium-phenyl used. The other fractions consist of approximately equal parts by weight of phenyl-trichlorosilane and triphenyl-chlorosilane.

EXAMPLE 4.

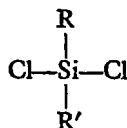
- Again in analogy with Example 1 a mixture of 700 g. methyltrichlorosilane and 300 g. diethyl ether is reacted at -30°C with 1 litre of the sodium-phenyl suspension. The yield of phenyl-methyl-dichlorosilane amounts to 78% referred to the sodium-phenyl used.

WHAT WE CLAIM IS:—

1. Process for the controlled production of a silane derivative of the general formula



- 25 in which R and R' (same or different) each represent chlorine, a phenyl radical or an alkyl or cycloalkyl radical having 1 to 24 carbon atoms, which comprises providing a solution of a silane derivative of the general formula



in an inert solvent, providing a suspension of sodium-phenyl in an inert dispersing medium in a concentration of at most 1

mol $\text{C}_6\text{H}_5\text{Na}$ per litre, cooling the silane derivative solution to a temperature of between -20 and -80°C whilst stirring vigorously, and simultaneously adding to the silane derivative solution an amount of the suspension stoichiometrically corresponding to the desired degree of phenylation, the addition of the suspension taking place evenly over a period of at least 30 minutes, and being effected in the absence of air and water.

2. Process as claimed in claim 1 wherein the silane derivative solution is provided by dissolving the silane derivative in at least an equal volume of the inert solvent.

3. Process as claimed in claim 1 or 2 wherein the silane derivative solution is cooled to a temperature of between -20 and -40°C .

4. Process as claimed in any of claims 1 to 3 wherein the addition of the suspension takes place over a period of 1 to 3 hours.

5. Process as claimed in any of claims 1 to 4 wherein the suspension is also cooled.

6. Process as claimed in any of claims 1 to 5 wherein the inert solvent is an aromatic, aliphatic or cycloaliphatic hydrocarbon, an electron donor, or a mixture thereof.

7. Process as claimed in any of claims 1 to 6 wherein the inert dispersing medium is an aromatic, aliphatic or cycloaliphatic hydrocarbon, an electron donor, or a mixture thereof, having a boiling point higher than the melting point of sodium.

8. Process as claimed in any of claims 1 to 7 wherein the reaction is carried out under an atmosphere of very pure nitrogen or argon.

9. Process for the controlled production of a silane derivative substantially as hereinbefore described in any of the Examples.

10. A silane derivative, whenever produced by a process as claimed in any of the preceding claims.

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